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Research paper

# Effect of temperature on the rheological properties of neat aqueous Wyoming sodium bentonite dispersions

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ABSTRACT

Temperature affects significantly the rheological behavior of neat water Wyoming Na-bentonite dispersions. The results of a very systematic study are presented regarding rheological measurements of 7% mass concentration at different temperatures, ranging between 25 and 80 °C at atmospheric pressure. Higher temperature increased the shear stresses at low shear rates while the effect was much smaller at higher shear rates. The Herschel-Bulkley rheological model fitted extremely well all data. The yield stress increased linearly with temperature by almost three-fold, the flow consistency index decreased exponentially with temperature by almost five-fold and the flow behavior index increased by about 20%, tending towards the Newtonian value. At low shear rates (<100 rpm corresponding to <170 1/s Newtonian shear rates), which represent very well the shear rates experienced by drilling fluids in the critical annulus region, all rheograms appeared fairly linear and the Bingham plastic model fitted well all data. The Bingham yield stress, from the low shear rate data, increased linearly with temperature, while the plastic viscosity decreased with temperature, in a manner very similar to the decrease of water viscosity with temperature. The plastic viscosity and Bingham yield stress data, from the low shear rate range, can be fitted well by an Arrhenius-type equation, with the activation energy for the plastic viscosity very similar to the activation energy for water viscosity, while for the Bingham yield stress, the activation energy is equal but opposite in sign to that of the plastic viscosity. A hypothesis is stated for the the observed linear increase of the yield stress with temperature, in the temperature range studied. One should be concerned when non-standard preparation and measurement procedures are followed which makes extremely difficult to understand any differences observed when reporting rheological data of water bentonite dispersions. A standard methodology is proposed, complementary to API, which can give very consistent results.



## 1. Introduction

Water bentonite dispersions have many unique properties, making bentonite a very important clay material for a multitude of processes. These dispersions are used in several industries, such as in the oil and gas industry for drilling applications, in pharmaceuticals, in paper making, in cosmetics, in wine making for clarification, etc.

Bentonite is an absorbent aluminium phyllo-silicate clay (i.e. made of several leaves, from Greek word 'φύλλο' = leaf) and it is a member of the smectite group of clays. Smectites are plate-like minerals with expanding lattices which when mixed with water form non-Newtonian dispersions. Bentonite is normally classified as sodium bentonite or calcium bentonite depending on the dominant cation in the crystal lattice and it has as major constituent montmorillonite.

Sodium montmorillonite particles are laminar in shape. They have a non-homogenously distributed surface electrical charge which distinguishes the faces and the edges of the clay platelets. The faces bear a permanent negative charge stemming from isomorphous substitution of $Si^{4+}$ and $Al^{3+}$ ions in the crystal lattice with lower valence cations like, $Na^{+}$, which is the prevalent one for the sodium montmorillonite used in drilling fluids. The edges are conditionally charged, that is, either positive or negative depending on the pH of the medium (van Olphen, 1977; Gray and Darley, 1988; Lagaly, 1989; Adachi et al., 1998). It is this imbalance in electrical charge between the faces and the edges of the bentonite particles that characterizes the types of interactions of clay particles with other substances.

In most of the applications of water bentonite dispersions, rheological characterization is required, because they are used in flow situations

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under a variety of environmental conditions of pressure and temperature, as well as in different geometrical shapes of the flow conduit, from the flow of drilling fluids in pipes and eccentric annuli, when drilling for oil and gas wells, to flow in rivers and hilly terrains in mud slides. Hence, considerable research is devoted to characterize rheologically such dispersions. However, most of the studies on the rheology of water bentonite dispersions were performed at room temperature. There exist few studies which investigated the effect of temperature and pressure on the rheological properties of bentonite dispersions (Hiller, 1963; Annis, 1967; Alderman et al., 1988; Briscoe et al., 1994; Kuru et al., 1998; Kelessidis et al., 2007a, 2007b). These studies were of great relevance to the drilling industry because of the extreme environments encountered in the past and nowadays when drilling for oil and gas in high temperature reservoirs and very deep wells.

Drilling fluid properties which have water as a base fluid and use bentonite for rheology control are greatly and negatively affected by temperature (Gray and Darley, 1988; Kelessidis et al., 2007a, 2007b). The degree of influence that temperature has should be known with good accuracy. However, because of the large number of variables involved, the behavior of bentonite dispersions at elevated temperatures is unpredictable and not fully understood. On the other hand, several studies, like for e.g. of Alderman et al. (1988), have shown that the effect of pressure on the rheology of water-based drilling fluids is minimal.

Temperature may influence the rheological properties of water-bentonite dispersions in a number of ways (Gray and Darley, 1988): (a) physically, because an increase in temperature decreases the viscosity of the liquid phase, (b) chemically, because all hydroxides react with clay minerals at temperatures above 90 °C; at low alkalinity, the effect on the rheological properties is not significant, but at high alkalinity, the effect may be severe and (c) electrochemically, because an increase in temperature increases both the ionic activity of any electrolyte and the solubility of any partially soluble salts that may be present in the dispersion. The resulting changes in ionic and base–exchange equilibria modify the balance between interparticle attractive and repulsive forces thus greatly affecting the degree of aggregation (flocculation) or dispersion of the bentonite particles in the water medium.

Hiller (1963), using raw Wyoming bentonite converted to sodium bentonite, examined the rheological behavior of 4% mass dispersions in the presence of electrolytes. He found that at low electrolyte concentration both plastic viscosity and yield stress decreased with increasing temperature (up to 176 °C) and increased slightly with pressure (up to 550 bar). However, at high electrolyte concentration an increase in yield stress and a decrease in plastic viscosity with increasing temperature were observed. Annis (1967), started with raw Wyoming bentonite which was treated to get sodium bentonite and prepared dispersions in water which became more shear thinning as temperature increased to 150 °C, giving higher yield values but lower plastic viscosities, computed from the high shear rate range (300 and 600 rpm viscometer speeds). Annis (1967) also observed that the decrease in plastic viscosity was similar to the decrease of water viscosity with temperature, thus higher temperatures essentially affected only the yield stress values. Using sodium-bentonite, with 85% montmorillonite and with $Na^{+}$/$Ca^{++}$ ratio of 1.71, in neat form and with additives, Alderman et al. (1988) found only a small effect of pressure on the rheological parameters, but found a continuous decrease of high shear rate viscosity with temperature, in a similar fashion to the decrease of water viscosity with temperature. The yield stress increased exponentially with temperature only after a characteristic temperature. Briscoe et al. (1994), found that, for 7 to 10% mass water - sodium based bentonite dispersions, the yield stress increased significantly with temperature while the plastic viscosity decreased significantly at temperatures up to 140 °C but it did not change appreciably with pressure (up to 1400 bar). Rossi et al. (1999) studied the effect of pressure and temperature on the rheology of sodium-montmorillonite dispersions which contained different electrolytes. They reported that an increase in temperature increased the yield stress because of thermal induced swelling. Santoyo et al. (2001) reported rheological measurements of typical water based drilling fluids (having four different bentonites containing mainly sodium-montmorillonite) used in geothermal drilling, which showed a small decrease of apparent viscosity up to temperatures between 80 °C to 120 °C and a drastic increase at temperatures >125 °C and up to 175 °C. Lin et al. (2016), reported rheological measurements of commercial kaolinite and commercial bentonite water dispersions, at 3 °C (close to seabed temperature) and at 25 °C and found that as temperature increased, the yield stress of these dispersions increased.

In all above studies most efforts focused on the development of appropriate additives to counteract the detrimental effect of temperature on the rheological properties of water bentonite dispersions and not so much on the understanding of the effect of temperatures of the neat dispersions (water and bentonite only) on their rheological properties and in particular of the yield stress.

The aggregation of individual bentonite particles which leads to flocculation of bentonite dispersions at high temperatures could be prevented with the addition of different additives, called thinners, like, polysaccharides, cellulosics, starches with polyglycols (von Oort et al., 1997), commercial anionic thinners (Rabaioli et al., 1993), synthetic polymers (Tehrani et al., 2009), or the use of metal complexes (Burrafato et al., 1995). Lignites are particularly effective, either complexed with metals (Hilscher and Clements, 1982; Nyland et al., 1988) or in neat form (Kelessidis et al., 2007a, 2007b, 2009). The latter investigators have attributed the beneficial effect of lignite, at the determined optimal 3% mass concentration, to the presence of humic components, noting, however, that complete understanding of this beneficial effect was still elusive.

Despite the known detrimental effects of temperature on the rheology of water-bentonite dispersions and the development of a large number of additives to counteract such effects, there are very few, if any, detailed studies focusing on the understanding of the mechanisms of bentonite platelet enhanced flocculation tendencies at higher temperatures which lead to very high yield stress values. This study is devoted to shed some additional light into the mechanisms of the bentonite inter particle interaction in high temperature environments, by combining macroscopic measurements (rheological measurements) with microscopic measurements (XRD, SEM, TEM, etc.) which can aid our understanding of the interactions of the particles in the microcosmos of such dispersions.

## 2. Materials and methods

Detailed description of materials and methods can be found in Vryzas et al. (2016) but here a brief description is given. The Wyoming sodiumbentonite (Aquagel-Gold Seal) was supplied by Halliburton in powder form with relative density of 2.6 and without any polymer additives, according to vendor specifications. It is tan in colour with a pH range 8–10. X-Ray Diffraction (XRD) (Fig. 1) confirmed that the major mineralogical component of the samples is sodium-montmorillonite. Minor phases like illite, muscovite, quartz, cristobalite, plagioclase (albite), gypsum and clinoptilolite zeolite are also present.

The sample components, as percent oxides, are shown in Table 1.

The mean particle size of bentonite was 36 μm (Vryzas et al., 2016). High-resolution transmission electron microscopy (HRTEM) images were obtained in a JEOL JEM 2010 microscope operating at 200 kV and equipped with an Oxford Instruments INCA EDS detector.

Wyoming sodium bentonite (45.16 g) was added to 600 ml of deionized water to give 7.0% mass concentration and mixed at high speed in a Hamilton Beach mixer for 20 min as per American Petroleum Institute (API) procedures (API, 2003). The dispersion was left to hydrate for 16 h in covered plastic containers. The pH range of all samples was between 7.8 and 8.2. All rheological measurements were taken one day after the initial sample preparation. Before making the rheological measurements the samples were stirred for 5 min in the Hamilton Beach mixer in order to achieve the same shear history for each sample (API, 2010). The preparation and measurement protocols for each

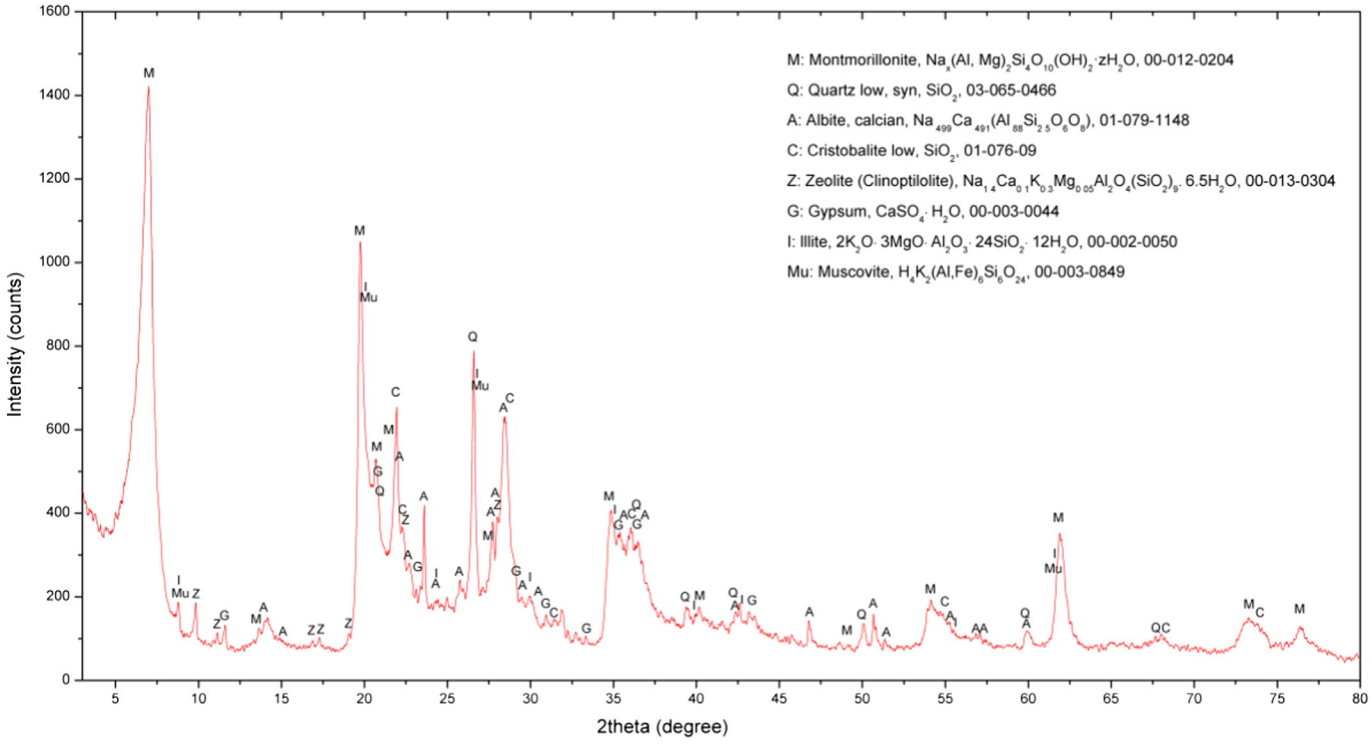


**Fig. 1.** X-Ray diffraction (XRD) of raw Wyoming sodium bentonite.

sample were followed strictly, in order to ensure consistency and to minimize any biases of our results.

Rheological measurements were performed at various temperatures (25 °C up to 80 °C) and ambient pressure, using a Couette type viscometer (Grace M3600). The radii of the fixed cylinder is 17.245 mm and of the rotating outer cylinder is 18.415 mm, thus giving a gap of 1.170 mm and an outer to inner diameter ratio of $\delta = 1.068$. The fixed cylinder has a height of 38.0 mm. Viscometric data were obtained at fixed speeds of 600, 300, 200, 100, 60, 30, 6, 3 rpm, which give Newtonian shear rates of 1021.38, 510.67, 340.46, 170.23, 102.14, 51.069, 10.21 and 5.11 $s^{-1}$, respectively (Kelessidis and Maglione, 2008a). The use of Newtonian shear rates for the rheological analysis of non-Newtonian fluids has been questioned (Kelessidis and Maglione, 2006a), and solutions incorporating the true shear rates for Herschel-Bulkley fluids have been reported (Kelessidis and Maglione, 2008b), however, the majority of analyses still uses Newtonian shear rates. In this work, and because the viscometer gap is fairly narrow, the use of Newtonian shear rates is a good estimate of the true shear rates. The yield stress is estimated from the obtained rheograms after extrapolating the shear stress – shear rate curve to zero shear rate and fitting an appropriate rheological model. The readings were taken from high to low speeds, while rotation lasted for 60s at each rotational speed, with readings being recorded every 10s, thus giving six measurements for each rotational speed with a total duration of 8 min per cycle. These six values were averaged and recorded. The rheological parameter estimation was performed according to the Herschel-Bulkley (HB) model,

$$\tau = \tau_y + K(\dot{\gamma})^n \tag{1}$$

**Table 1**
X-ray Fluorescence (XRF) compositional analysis (presented as oxides percent) of raw Wyoming sodium bentonite.

| Oxides | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $Na_2O$ | MgO | CaO | $K_2O$ | $TiO_2$ |
|---|---|---|---|---|---|---|---|---|
| Concentration, wt% | 65.30 | 20.30 | 5.75 | 2.38 | 2.24 | 1.30 | 0.66 | 0.23 |

where, $\tau, \dot{\gamma}$ are the shear stress and shear rate respectively, and the three Herschel-Bulkley rheological parameters are, the yield stress, $\tau_y$, the flow consistency index, $K$, which is an indication of viscosity, and the flow behavior index, $n$. The Herschel-Bulkley rheological model has proven to give the most accurate fitting results for water-bentonite dispersions used in these experiments. The Herschel-Bulkley rheological parameters were determined using non-linear fitting subroutines from suitable statistical package, like for e.g. Matlab™, or the excel (Solver™), using least squares fittings routines, and two statistical indicators, the sum of errors square, $SQ^2$, and the coefficient of determination, $R$,

$$SQ^2 = \sum_{i=1}^{N} (y_i - \hat{y}_i)^2 \tag{2}$$

and,

$$R = \sqrt{1 - \frac{SQ^2}{\sum_{i=1}^{N} (y_i - \bar{y})}} \tag{3}$$

where, $y_i$, is the measured parameter value, $\bar{y}$, is the mean value of the, $y_i$,s, $\hat{y}_i$, is the predicted (ith) value, and (N) is the total number of measured points, in this case N = 8.

Temperature was controlled using a circulating water bath capable of maintaining the desired temperature with an accuracy of ±0.5 °C. The water bath allowed the water to circulate around the viscometer cup while doing the rheological measurements. Preceding each test, we started the circulating water bath and waited until the desired temperature was reached. The gradual increase of temperature was performed at a rate of 1 °C/min. Once the desired water temperature was achieved, the sample was stirred for 5 min using the high speed mixer (Hamilton Beach) prior to each measurement, in order to achieve the same shear history. Then, the sample was poured into the measuring

**Table 2**
Sample preparation methodology comparison.

| Reference | Mixing | Mixing time | Bentonite hydration | High temperature | Pre-shearing | Time of pre-shearing |
|---|---|---|---|---|---|---|
| Alderman et al. (1988) | High speed | | | Hot roll, 100 °C, 48 h | | |
| Alderman et al., 1991 | High shear | Roll 100 rpm, 3 h | 16 h | | Cold roll, 100 rpm | 10 min |
| API | High shear | Total 15 min (5 + 10) | 24 h | | High shear | 5 min |
| Benna et al. (1999) | Sonicate | Roll 24 rpm, 24 h, leave for 13 days | Sonicate | | | |
| Briscoe et al. (1994) | High shear | | >1 day, static | | Restir | |
| Hilscher and Clements (1982) | | | Slow roll, 65.5 °C, 16 h | | High shear | 5 mins |
| Khandal and Tadros (1988) | High shear | 5–10 min, depending on clay concentration | none | | None | None |
| Laribi et al., 2006 | Overhead mixer (low shear) | 12–15 h | 5 days | | None | None |
| Miano and Rabaioli (1994) | Vigorously, Hamilton beach mixer | | 16 h | Hot roll, 16–24 h, 17 rpm | Low speed | 10 mins |
| Nyland et al. (1988) | Stirring | 1 h | | Hot roll 21 h, 121 °C | Stirring | 1 h |
| Penner and Lagaly (2000) | Ultrasound | 72 h shaking | | | | Ultrasound |
| Ramos-Tejada et al. (2001) | | | | | For 30s with 10 Pa shear stress | Measure after 3 min |
| Rossi et al. (1997) | High shear | Sufficient (not stating specific time) | Up to 24 h | | None | None |
| Singh and Sharma (1991) | | | 24–48 h | 204–232 °C, static, 16 h | | |
| Zhang and Yin (2002) | 10.000 rpm | 20 min | 24 h | | | |

cup and the experiment started immediately, with an initial step of rotation at 600 rpm for 200 s, before recording any values. This step was added in the experimental procedure in order to achieve a temperature equilibration of the sample. The temperature of the samples during the experiments was monitored with a temperature sensor embedded into the viscometer cup. Before starting the experiment the exact temperature of the sample inside the viscometer cup was also measured with an external thermometer in order to double check temperature accuracy. The measurements were done at five different temperatures and this was achieved with five different samples, prepared at the same time, and then performing the measurement as indicated above. When each test at the specific temperature finished, the tested sample was transferred to the closed container and the measurement of the next sample at the next temperature was performed, following the same procedures.

In order to avoid any evaporation effects on our results which could be significant at higher temperatures, although there is no reference which quantifies such effect, a 1.0 mm thick film of mineral oil, of 97.2 cP viscosity at 25 °C, supplied by Brookfield Ametek Inc., was carefully placed on the sample free surface, as per previous works (Laribi et al., 2006; Tehrani, 2008).

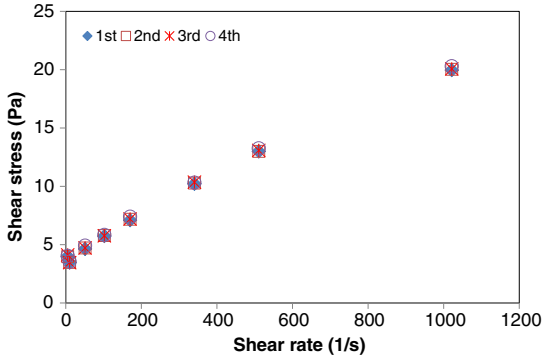


**Fig. 2.** Rheograms of four different samples of 7% mass Wyoming sodium bentonite water suspensions, prepared the same day and measured a day later, as per preparation methodology.

## 3. Consistency of sample preparation and measurement methodology

Any colloidal dispersion, like the ones studied here, exhibit peculiar flow characteristics and their rheological behavior depends strongly on prior shear history. The flow/rheological behavior of aqueous bentonite dispersions are governed by colloidal system chemistry fundamentals (van Olphen, 1977; Luckham and Rossi, 1999). The order of addition of agents in forming the dispersion is quite significant (Au and Leong, 2013). For example, water dispersions will have different properties if salt is added to water before or after the addition of bentonite. The physical state of the additives (liquid or solid) also influences the properties of the dispersion. In addition, mixing and preparation procedures such as, hydration, time of mixing, temperature, aging, are all significant influencing factors for the final properties of these dispersions.

It is very important to conduct experiments under similar conditions, if a comparison is to be made on results from different samples and between different laboratories, because of shear and time dependence of rheological properties of clay dispersions. The American Petroleum Institute (API) procedures and specifications (API Spec 13A, 2010; API Spec 13I, 2000; API Spec 13B-1, 2003) were developed in order to establish common procedures but sometimes these specifications do not deal with newer additives or newer requirements that are used or needed in different mud formulations that perform difficult tasks under varying conditions (Clark, 1995).

It is often very difficult to compare results from different investigators because mixing and preparation procedures are almost never the same. From a review of the literature and in order to have consistent

**Table 3**
Herschel-Bulkley rheological parameters of the four samples.

| Sample | $\tau_y, Pa$ | $K, Pas^n$ | $n$ | $R$ | $SQ^2, Pa^2$ |
|---|---|---|---|---|---|
| S1 | 3.36 | 0.0563 | 0.822 | 0.9992 | 0.35 |
| S2 | 3.36 | 0.0582 | 0.817 | 0.9994 | 0.29 |
| S3 | 3.40 | 0.0580 | 0.818 | 0.9990 | 0.47 |
| S4 | 3.44 | 0.0600 | 0.815 | 0.9993 | 0.31 |
| Mean value | 3.39 | 0.0580 | 0.818 | | |
| St. dev/mean | 1.1% | 2.8% | 0.4% | | |

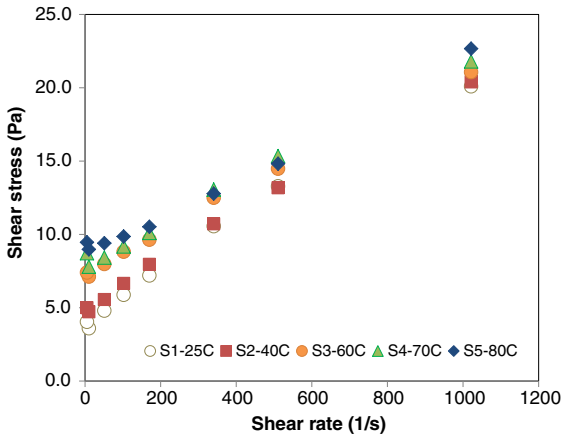


**Fig. 3.** Rheograms of 7% mass Wyoming sodium bentonite in water at different temperatures.

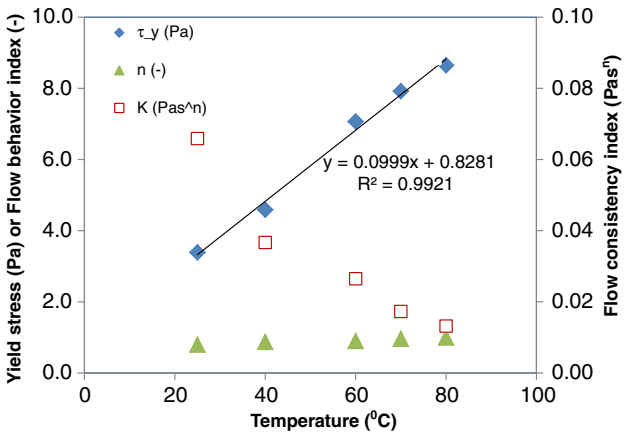


**Fig. 4.** Variation of the Herschel-Bulkley rheological parameters with temperature.

results, it is evident that the important parameters are: (1) the raw materials, (2) the mixing procedure of water and bentonite, (3) the mixing time, (4) the mixing energy, (5) the hydration of bentonite (static or dynamic), (6) the mixing procedure of any additive, (7) the hydration of any additive (static or dynamic), and (8) any pre-shearing done before measurement. Information about these procedures was sought in the literature and a non-exhaustive list of procedures that were followed is presented in Table 2. Wherever information is not indicated, it means that no actual reporting was made in the relevant reference.

From the inspection of the list it is evident that there is no consensus on the procedures of preparation of water-bentonite dispersions, and this is true for the listed works covering a period of >15 years. Drilling fluid industry appears to follow more 'common – API' procedures, though not fully, while 'bentonite or colloidal industry', if we can call it that, seems to follow less common and less standardized procedures. Caution should thus be exercised when comparing results of bentonite/colloidal dispersions among different, but also even within same, laboratories, because preparation procedures are very important for producing the desired rheological properties.

In this work, as well as other published work from our laboratory (Kelessidis et al., 2006b; Kelessidis et al., 2007a, 2007b; Kelessidis and Maglione, 2008a), we have followed API procedures and in cases where there were no procedures listed (Clark, 1995), we have followed the ones developed in our laboratory, as they have evolved over the many years dealing with such systems. It is our conclusion (Kelessidis, 2008) that following API procedures, and most importantly the procedure of preshearing, consistency in measurements is ensured, so that cross-comparison of results can be made with more certainty. Møller et al. (2006) have also recognized the importance of controlling the aging history of colloidal samples by large preshearing in getting reproducible results.

The consistency of the results, following API procedures and methodologies described above, is proven from the results presented in Fig. 2, where the rheograms of four different water-bentonite dispersions are plotted. These samples were prepared in four different batches and measured at 25 °C, at different times. The exact replication of these rheograms is, if anything else, remarkable. Data fitting to the Herschel-Bulkley rheological model, gave the results shown in Table 3.

It is worth noting the following: (a) the excellent fit of the data to the Herschel-Bulkley rheological model, with extremely small error square values; (b) the remarkable repeatability of the flow behavior index, ($n$), hovering around 0.82; (c) the very good repeatability of the yield stress at 3.36–3.44 Pa, with a standard deviation of only 1.1% of the mean value, and (d) the somewhat more fluctuation of the flow consistency index, $K$, which should be investigated further, as this may give some clues about the particle-to-particle interaction contributing to the value of the bulk viscosity.

**Table 4**
Herschel-Bulkley rheological parameters of 7% mass water-Wyoming sodium bentonite suspensions at different temperatures.

| Sample | Temperature (°C) | $\tau_y (Pa)$ | $K (Pas^n)$ | $n$ | $R$ | $Q^2 (Pa^2)$ |
|---|---|---|---|---|---|---|
| S1 | 25 | 3.39 | 0.0659 | 0.800 | 0.9991 | 0.40 |
| S2 | 40 | 4.59 | 0.0367 | 0.876 | 0.9996 | 0.14 |
| S3 | 60 | 7.07 | 0.0265 | 0.905 | 0.9994 | 0.18 |
| S4 | 70 | 7.92 | 0.0173 | 0.966 | 0.9970 | 0.99 |
| S5 | 80 | 8.65 | 0.0132 | 1.000 | 0.9901 | 1.50 |

## 4. Temperature effect on rheological properties

In Fig. 3 the rheograms of all five samples at the tested temperatures are plotted. At low shear rates, the shear stresses increase when temperature increases, while at high shear rates, there is convergence of the shear stresses towards similar values, at least for the temperatures tested. The Herschel-Bulkley model was found to fit all sample rheograms very well and the rheological parameters together with the two statistical parameters, are shown in Table 4.

We notice an increase of yield stress with temperature, a decrease of the flow consistency index with temperature, while the flow behavior index increases with temperature and tends towards the value of 1.0, indicating that the dispersions become Bingham plastic at higher temperatures. We show the variation of the Herschel-Bulkley rheological parameters with temperature in Fig. 4. The yield stress increases almost perfectly linearly with temperature for the temperatures studied (the equation and regression coefficient are shown in the Figure). The flow

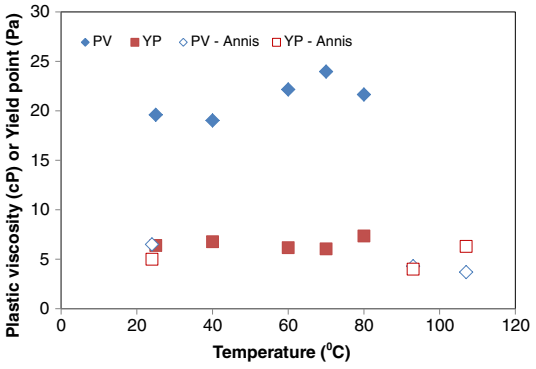


**Fig. 5.** Variation of plastic viscosity and yield point, determined from high shear rates (600 and 300 rpm), with temperature.

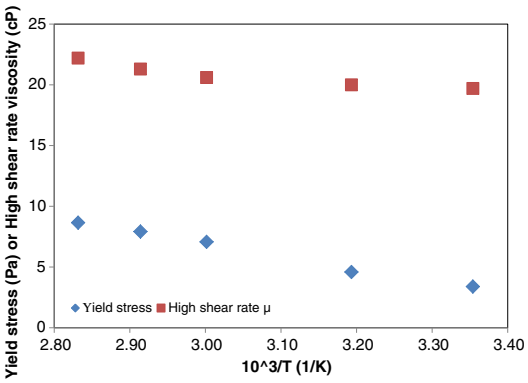


**Fig. 6.** Variation of the yield stress and of high shear viscosity (μ) with temperature, given in the form of Alderman et al. (1988).

consistency index decreases with temperature in an exponential manner, as,

$$K * 1000 = 126.6 * \exp(-0.028t), \quad (4)$$

where $t$ and $K$ are in °C and $Pas^n$ respectively. Water viscosity data of Kestin et al. (1978) gives the following dependence on temperature of water viscosity, $\mu_w$,

$$\mu_w * 1000 = 1.31 * \exp(-0.017t), \quad (5)$$

where $t$ and $\mu_w$ are in °C and $Pas$ respectively.

One observes that the exponential decrease of the flow consistency index of these dispersions is not exactly similar to the exponential decrease of the water viscosity, but it decreases much faster. This could be the result of the presence of bentonite particles which impart, at this concentration, not only the non-Newtonian behavior, but also the non-linear rheological behavior over the whole shear rate range that was investigated. Thus, the flow consistency index is not directly related to the viscosity of the base fluid, and more research is needed in order to better understand the non-linear rheological behavior of such systems.

The flow behavior index increases by about 20% from room temperature to the maximum tested temperature of 80 °C and trends towards the value of 1.0, in an almost linear fashion.

One can compute the plastic viscosity (PV) and the yield point (YP), using only the 600 rpm and the 300 rpm data (i.e. the high end shear rate range), as it is normally done by drilling industry for many years, and then plot these versus temperature (Fig. 5). Both yield point and plastic viscosity do not show any particular trend with temperature, at least for the tested temperatures of 25 °C up to 80 °C. In the same Figure we have plotted the three data points from Annis (1967) for comparison of the trends, although different mass fraction of Wyoming sodium

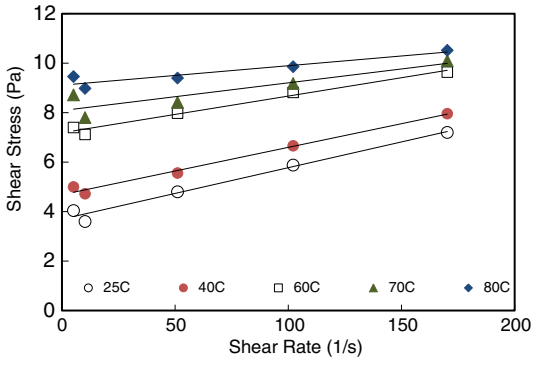


**Fig. 7.** Rheograms of Fig. (3), but only for lower shear rates (up to 170 1/s).

**Table 5**
Bingham plastic rheological parameters of 7% mass water-Wyoming sodium bentonite suspensions at different temperatures, for the low shear rate range (up to 100 rpm).

| Sample | Temperature (°C) | $\tau_{yBp}(Pa)$ | $\mu_p(Pas)$ | $R^2$ | $SQ^2(Pa^2)$ |
|---|---|---|---|---|---|
| S1 | 25 | 3.69 | 0.0208 | 0.9813 | 0.15 |
| S2 | 40 | 4.68 | 0.0191 | 0.9882 | 0.08 |
| S3 | 60 | 7.19 | 0.0148 | 0.9798 | 0.09 |
| S4 | 70 | 8.08 | 0.0112 | 0.8106 | 0.56 |
| S5 | 80 | 9.11 | 0.0079 | 0.8809 | 0.16 |

bentonite was used (5.14% mass). Annis data show a slight decrease of plastic viscosity and a tendency for an increase of the yield point.

One should compare the 'indifference' in the trends of either the PV or the YP, both from our data as well as the data of Annis (1967), with the excellent trends observed for all three rheological parameters of the Herschel-Bulkley model derived by utilizing all 8 rheological data points (Fig. 4). This comparison concretely proves that very wrong conclusions could be derived if utilization is made of only the high shear rate range of the rheological data with respect to the effect of temperature, at least for the neat water-bentonite dispersions.

Alderman et al. (1988) showed that the high shear rate viscosity (calculated at the maximum shear rate studied) could be correlated to (1/T), where T is the absolute temperature, and that it decreased with temperature in a similar fashion to the decrease of water viscosity with temperature. The yield stress, however, did not change appreciably until a characteristic temperature, and then it increased exponentially with increasing temperature (decrease in 1/T). However, they could not provide sufficient interpretation for this characteristic temperature. In Fig. 6 we present our data for the yield stress values and for the high shear rate viscosity, μ, calculated as $\tau/\dot{\gamma}$, at the maximum shear rate used in this study of $\dot{\gamma} = 1021\,(1/s)$. Both the yield stress and the high shear rate viscosity increased continuously and almost linearly with increasing temperature (smaller 1/T), in contrast to what Alderman et al. (1988) have reported. The reasons for the observed differences are not understood. One can note, however, that the particular trend reported by Alderman et al. (1988) was for a sample of unknown formulation, it was an unweighted mud (no barite added), but no further indication was given of any other additives (of the many utilized in their study), nor was the concentration of bentonite listed, while the dispersions used in this work were only of 7% mass of neat Wyoming sodium bentonite in water.

From the data in Fig. 3, the non-linearity of the rheogram curves stems mainly when we combine the low shear rate data (<100 rpm, corresponding to Newtonian shear rates of <170 1/s) with the high shear rate data (>200 rpm). It would be interesting to examine the low shear rate part and see if one can deduce some information regarding trends of the rheological parameters with respect to increasing

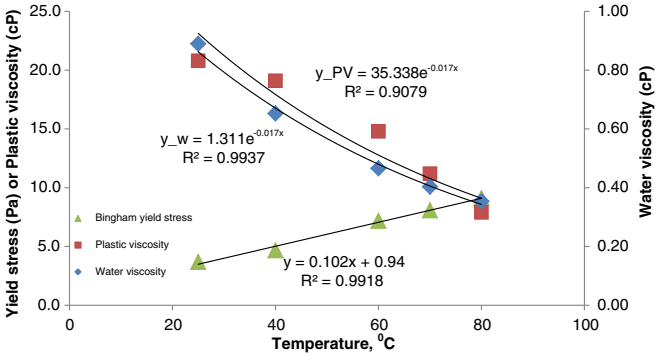


**Fig. 8.** Variation of Bingham yield stress and plastic viscosity with temperature (for low shear rate data up to 170 1/s).

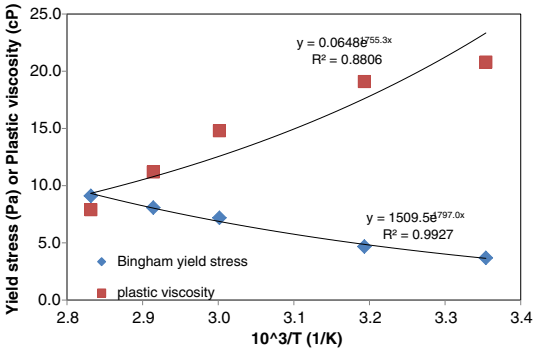


**Fig. 9.** Arrhenius-type plot for plastic viscosity and Bingham yield stress, for low shear rate values.

temperatures, because it is in the low shear rate range that the maximum effect of temperature was observed. Thus, restricting the analysis to the data set of (3, 6, 30, 60, 100 rpm), one can get the rheograms of Fig. 7. The rheograms are fairly linear for this low shear rate range, and hence, a Bingham plastic model can be fitted. The appropriate Bingham plastic rheological parameters, the Bingham plastic yield stress, $\tau_{yBp}$, and the plastic viscosity, $\mu_p$, as well as the two statistical correlators, the regression coefficient, $R^2$, and the sum of errors squared, $SQ^2$, are given in Table 5. The changes versus temperature, of the Bingham yield stresses and of plastic viscosities, so determined at low shear rate ranges, are shown in Fig. 8.

One observes similar linear increase of the Bingham yield stress with temperature, as with the Herschel-Bulkley yield stress, (Fig. 4), with the trend now given by,

$$\tau_{yBp} = 0.94 + 0.102(t), \tag{6}$$

where $(t)$ is the temperature, in degrees Celsius, and, $\tau_{yBp}$, is the Bingham yield stress, from the low shear rate data, in Pa. The plastic viscosity for the low shear rate data, $\mu_p$, decreases exponentially with temperature, as,

$$\mu_p * 1000 = 35.338 * \exp(-0.017 * t), \tag{7}$$

where $t$, is in °C and, $\mu_p$, in *Pas*.

In Fig. 8 the change of water viscosity with temperature is also plotted over this temperature range, from Eq. (5) above. It is noticeable that the decreasing trend of the water viscosity is exactly the same as of the low shear rate plastic viscosity, with the same exponential decay coefficient of $(-0.017)$ with the equation for the plastic viscosity having a higher multiplier. This indicates that the observed decrease in plastic viscosity, deduced from low shear rate range data, is mainly associated with the base fluid (water) decrease of viscosity with temperature, but with an enhanced factor (for this case of ~27 = 35.338/1.311), which should be the effect of the presence of bentonite increasing the plastic viscosity of the dispersion. It was stated above that a larger decay coefficient, of 0.028, was observed for the flow consistency index, $K$, (Eq. (4)), and the reason for such a difference should be further investigated.

An Arrhenius-type equation for the change of the plastic viscosity with temperature can be fitted and then the plastic viscosity data versus 1/T, where T is the absolute temperature can be plotted (Fig. 9). A much better representation of the plastic viscosity decrease with temperature is thus obtained when compared to the high shear viscosity (above, Fig. 6).

The resulting equation for the plastic viscosity, $\mu_p$, in *Pas*, written in an Arrhenius-type form, is,

$$\mu_p * 1000 = 0.0648 \exp(1755.3/T) = 0.0648 \exp\left(\frac{E_{a,PV}}{R_G T}\right), \tag{8}$$

hence,

$$E_{a,PV} = (1755.3)(8.314 \text{ J/molK}) = 14594 \text{ J/mol}, \tag{9}$$

where, $E_{a,PV}$, is the activation energy for the plastic viscosity derived from the low shear rate values, and, $R_G$, is the gas constant.

The Arrhenius-type dependence on temperature of the yield stress of Bingham plastic model, $\tau_{yBp}$, in *Pa*, is shown in Fig. 9 and it is given by,

$$\tau_{yBp} = 1509.5 \exp(-1797/T) = 1509.5 \exp(E_{a,\tau_{yBp}}/R_G T), \tag{10}$$

hence,

$$E_{a,\tau_{yBp}} = -14940 \text{ J/mol}, \tag{11}$$

where, $E_{a,\tau_{yBp}}$, is the activation energy for the Bingham yield stress. Alderman et al. (1988) have indicated that activation energies for the high shear rate viscosity of all drilling fluids they studied ranged between 9768 J/mol and 19,373 J/mol, encompassing water activation energy, which, however, as reported by different investigators, appears to have different values. For example, Alderman et al. (1988) reported the activation energy of the water viscosity, $E_{a,\mu w}$, to be equal to 13,838 J/mol, while Rohindra et al. (2012) lists a value for water of ~ 15,000 J/mol. Ouerfelli et al. (2012) indicate that, from a range of sources as well as their own data, $E_{a,\mu w}$, for pure water viscosity is not constant over a range of temperatures, rather it depends on $T$ and from their data, water viscosity activation energy was reported to be between 14,000 to 16,000 J/mol. Thus approximate values for water viscosity activation energy can be considered to be in the range of 13,000 to 16,000 J/mol.

Our measurements show that the activation energy for the plastic viscosity, derived from low shear rate values, for the water-bentonite dispersions studied, is similar to that of pure water, at least for the temperature range for which these experiments were performed, while the activation energy for the Bingham yield stress is almost equal in magnitude but opposite in sign. Whether this is a pure coincidence or whether

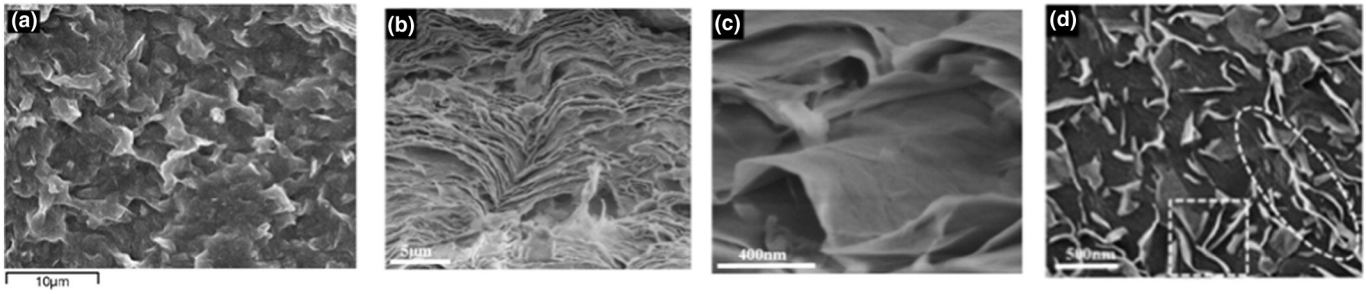


**Fig. 10.** SEM images of (a) Na-bentonite suspension of 6.41% mass at pH = 9.1 (Kelessidis et al., 2007c); (b, c, d) different magnifications of 5% mass suspension of sodium montmorillonite (derived from Swy-2 Wyoming bentonite, after Mouzon et al., 2016).

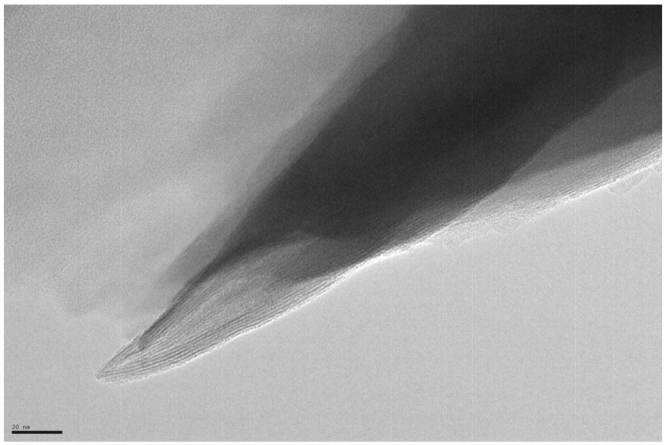

**Fig. 11.** TEM picture of 7% mass Wyoming sodium bentonite suspension. The individual platelets are clearly seen as the edges have folded, and one can count approximately 20 platelets (bar size = 20 nm), with approximately 1 nm thickness.

it has a physical meaning and could be an indirect proof of data consistency deserves further investigation.

## 5. Yield stress of bentonite dispersions

In the effort to understand the effect of temperature on the yield stress of water bentonite dispersions, we need to understand which are the factors behind the development of the yield stress of such dispersions. And while there has been a much debated discussion about the existence or not of the yield stress (Hartnett and Hu, 1989; Astarita, 1990; Barnes, 1999), we side with several investigators who believe the yield stress is an engineering reality (Kelessidis et al., 2006b) and it is developed in particular dispersions, such as the ones examined in this work, within the time frame of our observations and of applications of interest.

Sodium montmorillonite particles are plate like particles with very thin edges. Their faces are negatively charged while their edges are positively charged in acidic medium and negatively charged in alkaline medium (Tombacz and Szekeres, 2004; Lagaly and Ziesmer, 2003). The pH value at which the charge of the edges changes sign is the isoelectric point (IEP). While there is ambiguity on the exact value of the IEP, it may be taken at values of pH between 5 and 7 (Benna et al., 1999; Missana and Adell, 2000). This means that for the case of neat bentonite water dispersions, like the ones studied here, as well as of all drilling fluid formulations for which pH is alkaline, the edges of the bentonite particles are negatively charged. The majority of researchers postulate that gelation results from edge-to-face contacts (EF), particularly in acidic environments and in dilute dispersions, from face-to-face contacts, and from edge-to-edge (EE) contacts, especially at high clay content (Norrish, 1954; van Olphen, 1977; Luckham and Rossi, 1999; Lagaly and Ziesmer, 2003). Edge-to-face or edge-to-edge association leads to card-house like structures, while, face-to-face association leads to thicker and larger flakes (bands or tactoids, but the mechanism of formation of bands between negatively charges surfaces has not been explained.

The differences of postulations regarding particle association may be due to differences in particle size distributions, in chemical compositions, in the type of minerals present, because these materials come from different parts around the world. It may be for the same reasons that, still to date, researchers are not in agreement whether, bentonite platelets, upon dispersion in water, dissociate fully or not. Furthermore, these geometric associations (EE, EF, FF) are very idealistic particularly in view of previous observations (Kelessidis et al., 2007c) as well as of new results which show pictures, taken using more sophisticated instruments (Mouzon et al., 2016), of sodium-montmorillonite particles, derived from Swy-2 Wyoming bentonite, at high mass concentration, which are flexed and stack in layers, or tactoids, and associate in a 'face-to-face' configuration while some of the platelets associate in 'edge-to-face' manner, forming plausibly associations of Y-type (Fig. 10). Mouzon et al. (2016) also identified individual platelets which were fully dispersed.

In Fig. 11, a high resolution TEM image is shown, which was taken from one of the dried samples of water dispersions containing 7% mass of Wyoming sodium-bentonite used in this work. The existence of a tactoid is very evident, which consists of approximately 20 platelets, each of almost 1.0 nm-thickness. Similar TEM images to that of Fig. 11, exhibiting striking similarities were reported by Segad et al. (2012) and by Bailey et al. (2015).

One may argue that at high shear rates, the platelets will align with the flow direction and there will be less structure compared to the structured FF arrangement, when no flow, offering less resistance, hence one should observe smaller apparent viscosities, and in fact we have seen that they behave like Bingham plastics. As the shear rate is decreased, moving towards smaller shear rates, the particles re-align as per FF of flexed particles and thus offer more resistance to flow due to drag, resulting in an increase of the apparent viscosity. At the limit of no shear rate, the dispersion is at rest and the platelets associate mostly as per Mouzon et al. (2016) and Kelessidis et al. (2007c) pictures (Fig. 10). Thus, in order to initiate flow, we need extra force to apply for it to start moving, hence the manifestation of the yield stress.

It was demonstrated in this work, that higher temperatures result in higher yield stresses. Mouzon et al. (2016) showed that some of the platelets remain in dispersed state, even at 5% mass concentration, and not all platelets had this peculiar flexed FF structure. It is conceivable that as temperature increases, the particles in the dispersed state move due to Brownian motion and become also flexed and associate in the FF mode. The higher temperatures may also increase the frequency of the cluster breakdown, but conceivably, there is an equilibrium at which the number of cluster (FF) formation is larger than number of the cluster breakdowns, resulting in an increase of the yield stress. One may further argue that this increased FF association of the single particles is proportional to the heat input (i.e. increasing temperature), hence it could explain the observed linear increase of the yield stress with temperature, either the Herschel-Bulkley yield stress, or the Bingham yield stress, derived from low shear rates.

In Fig. 12 the SEM pictures of water- Wyoming sodium bentonite dispersions at 7% mass concentration are shown, taken from dried samples of the dispersions used in this work, after being exposed to 25 °C, 40 °C, and 60 °C, (after performing the rheological measurements at the indicated temperatures), while also showing SEM picture of the dry Wyoming sodium bentonite powder (Vryzas et al., 2016). The increase of the number of clusters as temperature increases is evident, and this was probably manifested as higher yield stresses observed at higher temperatures. This is consistent with published results (Chang and Leong, 2014) which showed increasing yield stress of aged dispersions with increasing particle size.

## 6. Conclusions

The rheology of the dispersions of 7% mass Wyoming sodium bentonite concentration can be modeled extremely well by the Herschel-Bulkley model, over the entire shear rate range and for all temperatures studied.

At low shear rates, the shear stresses increase significantly with temperature, with almost doubling of the shear stresses at the lowest shear rate measured. At high shear rates, the temperature effect diminishes and the shear stresses converge to similar values.

The yield stress increased linearly with temperature, a result not reported in the past, to the best of authors' knowledge. The flow consistency index decreased exponentially by a factor of almost five, while

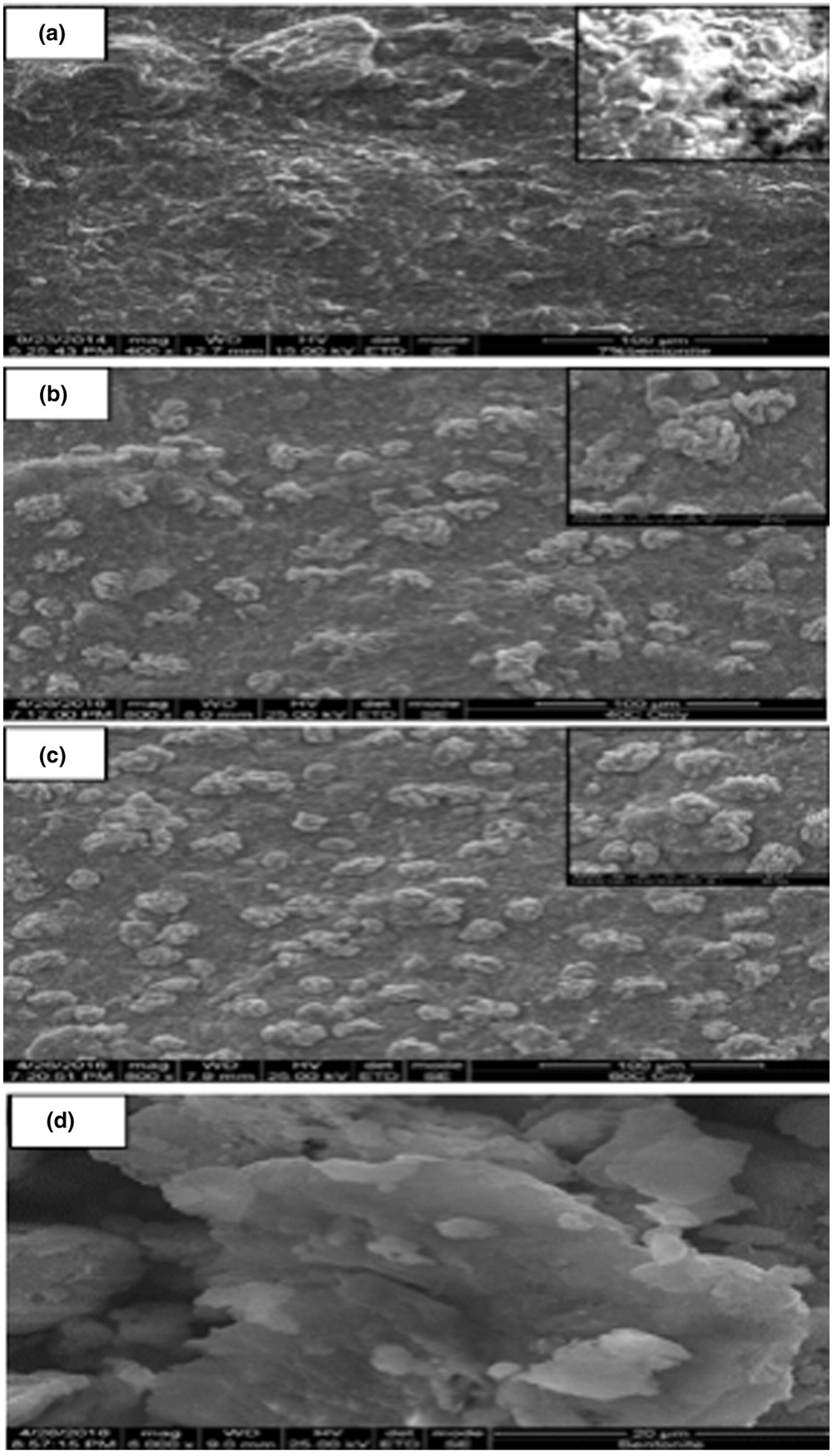


**Fig. 12.** SEM images, at 100 μm and insets at 40 μm, of dried samples taken from Wyoming sodium bentonite suspensions at respective temperatures, from top to bottom: (a) at 25 °C, (b) at 40 °C, (c) at 60 °C; and (d) Wyoming sodium bentonite powder at 20 μm (from Vryzas et al., 2016).

the flow behavior index increased by about 20% tending towards the Newtonian value.

Use of the plastic viscosity and of the yield point, as computed from the two high shear rates (300 and 600 rpm), done consistently by drilling industry, does not reveal the significant effect that temperature has on the rheological parameters.

Most of the change of the shear stresses with temperature occurs at low shear rates (<170 1/s), and the analysis of this work showed that at these low shear rates, all rheograms could be fitted well with the linear Bingham plastic model. The plastic viscosity, from the low shear rate range, decreased exponentially, in exactly the same manner as the base fluid (water) viscosity, while the Bingham yield stress increased linearly with temperature.

The plastic viscosity decrease was found to follow an Arrhenius-type dependence on absolute temperature, with activation energies very close to the activation energies for water viscosity. The Bingham yield stress had also Arrhenius-type dependence, with similar value of activation energy to that for plastic viscosity, but opposite in sign.

It is postulated that, as temperature is increased, the individual flexed particles, not in FF association, identified and reported by other researchers, associate with the tactoids or with each other, forming additional tactoids, thus increasing the yield stress as temperature increases.

The requirements to get consistent rheological results, a very difficult task for such colloidal dispersions, were identified, and preparation and measurement procedures, complementary to API procedures, were proposed, presenting also evidence of consistency in the form of extremely repeatable results.

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